Mathematical model for a radioactive marker in silicide formation

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A mathematical model is constructed to interpret the profiles of radioactive ^{31}Si tracers in a computer simulation proposed by R. Pretorius and A. P. Botha [Thin Solid Films **91**, 99 (1982)]. This model assumes that only Si moves in the silicide, that the Si moves interstitially and convectively, and that the moving Si can exchange sites with the stationary Si in the silicide lattice. An analytical solution of this model is given and confirms the published computer simulation data. However, it is shown that the model is physically inadequate. Solutions of another model which assumes that metal, instead of Si, is the moving species for silicide formation (either interstitially, or substitutionally, or both), with self-diffusion of ^{31}Si in the silicide during silicide formation. Almost all the experimental data can be fitted by solutions of both models. These examples demonstrate that radioactive tracer experiments alone are insufficient to determine the moving species when a solid binary compound film forms by reaction of adjacent elemental layers. Both inert marker and tracer data are needed to identify the moving species and the mechanisms.

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I. INTRODUCTION

Metal silicides are important as ohmic contacts and Schottky barriers in silicon devices. Extensive studies have been performed to obtain an understanding of the formation of silicides. The identification of the dominant moving species for silicide formation[1] during growth of the silicide layers is one of the basic questions. Experimentally, the problem can be approached with marker and tracer studies. Elements that have been used include noble gas such as Xe and Ar (Refs. 2–5), reactive elements such as oxygen,[6,7] thin inert metal layers,[8] and a metal with properties similar to that contained in the silicide.[9–11] All these experiments have the major disadvantage that foreign elements are introduced into the system. Those foreign atoms may affect the diffusion mechanism and the reaction kinetics. Therefore radioactive isotopes of the constituent elements, such as ^{31}Si and ^{56}Ni (Refs. 12–18) are uniquely clean indicators. However, the correct interpretation of the results obtained from these tracer experiments requires careful comparison with mathematical models. For this purpose, Pretorius *et al.* have used simple computer simulations to calculate ^{31}Si tracer profiles [19] in metal silicides. Although the profile of simulation fits that of experiment very well, such simulations provide limited physical insight. We have therefore, by using the same assumptions used in simulation, constructed a mathematical model (the first model) to interpret the simulation profiles. The analytical solution of this model confirms the simulation data but it is also shown that this model represents the physical situation as an approximation only. A second solution is also given for a very different physical model (the second model) that fits the experimental data equally well.

II. METHOD

Experimentally, the kinetics of metal silicide formation tend to be controlled either by an interfacial reaction [interfacial reaction controlled (IRC) silicide] where the growth is a linear function of time (e.g., $CrSi_2$), or by diffusive transport [diffusion controlled (DC) silicide] where the growth is proportional to the square root of time (e.g., PtSi).[20] We therefore consider only these two cases for our model.

We will consider a sample prepared with a uniform layer of R atoms per unit area of ^{31}Si (i.e., of thickness R/N, where N is the atomic density of Si) on a nonradioactive Si (^{n}Si) substrate, with a layer of metal on top. A schematic representation of this sample is shown in Fig. 1(a). We assume that a single-phase silicide layer of uniform thickness grows between the Si and the metal and that sufficient metal is present to consume all the ^{31}Si and some ^{n}Si from the substrate (see Fig. 1). We will develop one-dimensional models with the origin of position ($x = 0$) at the Si/silicide interface for the first model, and at the metal/silicide interface for the second model. Positive x is chosen to be on the side of the silicide. We define the origin of time ($t = 0$) when the silicide begins to form.

We define the following quantities:

n	= atom density of Si in the Si sublattice of silicide ("fixed Si") (Si atoms/cm^3).
$a_n(x,t)$	= fraction of ^{31}Si in n at x, t—referred to as "activity" of fixed Si, or as "fixed activity."
x_0	$= R/n$ (cm).
t_0	= the time when all the ^{31}Si in the substrate has been transformed to silicide (s).
$w(t)$	= thickness of silicide at time t (cm).
l	= thickness of silicide after complete reaction of the metal layer (cm).
X	$= x/x_0$.
L	$= l/x_0$.

A. Model 1

In this model we assume that:

(A1) Si is the only moving species during silicide formation.

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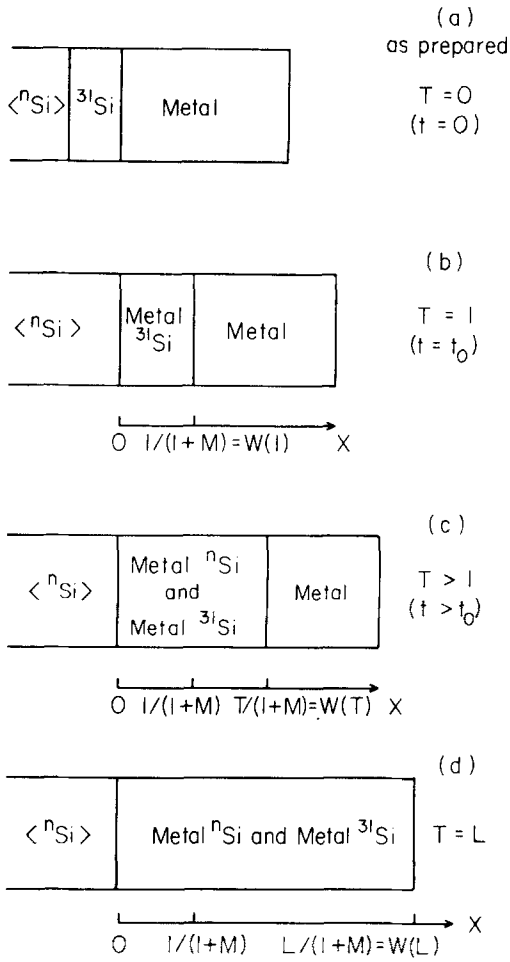

FIG. 1. Schematic representation of ^{31}Si marker sample. (a) As-prepared sample with R atoms of ^{31}Si per unit area deposited between ^{n}Si substrate and metal. (b) At $t = t_0$ (i.e., $T = 1$) the last ^{31}Si is just passing through Si/silicide interface, the silicide thickness is $x/(1+M)$. (c) Case for $t > t_0$ (i.e., $T > 1$). (d) At $T = L$ the metal is totally consumed.

(A2) Si atoms move interstitially from the Si substrate through the silicide and form additional silicide with the metal at the silicide/metal interface.

(A3) Si atoms pass through the silicide convectively, i.e., thermal random motion of Si is ignored.

(A4) In passing through the silicide, a moving Si atom can exchange positions with a Si atom that is bonded to metal atoms in the silicide lattice.

(A5) Si atoms that are bound to the silicide lattice are fixed in space (fixed Si).

(A6) Silicide forms at the metal/silicide interface with equal probability for ^{31}Si and ^{n}Si.

We define the following quantities:

$m(x,t)$ = atom density of mobile Si at x,t (Si atoms/cm^3).

$a_m(x,t)$ = fraction of ^{31}Si in $m(x,t)$—referred to as the "activity" of moving Si, or as "mobile activity."

$f(x,t)$ = flux of Si atoms at x,t [Si atoms/(cm^2 s)].

λ^{-1} = probability per unit length that a moving Si atom exchanges position with a stationary Si atom in the Si sublattice of silicide (cm^{-1}).

c = mean distance between fixed Si atoms in the silicide ($\approx$Si sublattice constant/$k^{1/3}$), where k is number of Si atoms per unit cell (cm).

$p(d,\lambda)$ = the fractional change of the integrated fixed activity of a layer of finite thickness d of silicide made up initially of pure ^{31}Si after a flux of pure ^{n}Si has passed whose integrated flux equals the amount of Si in that silicide layer.

To model the motion of the ^{31}Si as the silicide grows, we note that at any point x in the silicide at time t, there are two particle fluxes, namely the flux of radioactively traced ^{31}Si, $f(x,t)a_m(x,t)$, and the flux of nonradioactive Si, $f(x,t)[1-a_m(x,t)]$. Particles are conserved for each flux separately, so that there are two continuity equations:

$$\frac{\partial[f(x,t)a_m(x,t)]}{\partial x} = -\frac{\partial[na_n(x,t)]}{\partial t} - \frac{\partial[m(x,t)a_m(x,t)]}{\partial t} \tag{1}$$

and

$$\frac{\partial f(x,t)[1-a_m(x,t)]}{\partial x} = -\frac{\partial n[1-a_n(x,t)]}{\partial t} - \frac{\partial m(x,t)[1-a_m(x,t)]}{\partial t}. \tag{2}$$

The sum of these two equations gives the continuity equation of the total moving Si:

$$\frac{\partial f(x,t)}{\partial x} = -\frac{\partial m(x,t)}{\partial t}. \tag{3}$$

Using Eq. (3), we can simplify Eq. (1) to

$$f(x,t)\frac{\partial a_m(x,t)}{\partial x} = -n\frac{\partial a_n(x,t)}{\partial t} - m(x,t)\frac{\partial a_m(x,t)}{\partial t}. \tag{4}$$

The stationary Si in the silicide has no flux, but its radioactive and nonradioactive components can vary in time by exchange with the flux of moving particles. Consider the total number of fixed ^{31}Si in $(x,x+dx)$ at time t, which is $na_n(x,t)dx$. After a time interval dt, this quantity will be altered by the exchange between moving and fixed Si. If dx is so small that an exchange can occur at most once (i.e., $dx/\lambda \ll 1$), then the change in the number of fixed ^{31}Si atoms in $(x,x+dx)$ can be written as

$$dx[na_n(x,t+dt) - na_n(x,t)] = [1-a_n(x,t)]f(x,t)dta_m(x,t)dx/\lambda - a_n(x,t)f(x,t)dt[1-a_m(x,t)]dx/\lambda. \tag{5}$$

The first term on the right-hand side arises from exchange betwen fixed ^{n}Si and moving ^{31}Si, while the second term treats exchange between fixed ^{31}Si and moving ^{n}Si. This equation reduces to

$$\frac{\partial[na_n(x,t)]}{\partial t} = [a_m(x,t) - a_n(x,t)]f(x,t)/\lambda. \tag{6}$$

There is only one independent relation of this type be-

cause the sum of both components, $[a+(1-a)]n$, is fixed. Equations (3), (4), and (6) contain the four unknowns: $f(x,t)$, $m(x,t)$, $a_m(x,t)$, and $a_n(x,t)$. To specify a solution, one additional relationship between these unknowns must be provided.

It is convenient at this point to introduce some normalized quantities, symbolized with capital letters:

$M(x,t) = m(x,t)/n$.
$T = t/t_0$ for IRC silicides and
$T = \sqrt{t/t_0}$ for DC silicides.
$A_n(X,T) = a_n(x,t)$.
$A_m(X,T) = a_m(x,t)$.
$W(T) = w(t)/x_0$.
$E = x_0/\lambda$, exponent in the probability $\exp(-x_0/\lambda)$ that an atom traverses a thickness x_0 without exchange.

We point out that:

(1) Experiments show that the silicides are always very nearly stoichiometric during their formation, this fact implies that $M(x,t) \ll 1$.

(2) In the case of an IRC silicide, $m(x,t)$ and $f(x,t)$ are constants for all $w(t) > x > 0$ and $t > 0$ at steady state. From this, it is easy to prove that $f(x,t) = x_0 n/t_0 = f$.

(3) In the case of a DC silicide, $f(x,t)\sqrt{t}$ is a constant for all $w(t) > x > 0$ and $t > 0$ at steady state. From this, it is easy to prove that $f(x,t)\sqrt{t} = 0.5nx_0/\sqrt{t_0} = g$.

(4) As explained in Appendix II the probability $p(d,\lambda)$ is a function of d/λ, i.e., $p(d,\lambda) = p(d/\lambda)$ with properties: $p(d/\lambda) = d/\lambda$ for $d/\lambda \ll 1$ and $p(d/\lambda) = 1 - \sqrt{\lambda/(\pi d)}$ for $d/\lambda \gg 1$.

For simplicity, we will assume that steady state prevails, which is consistent with experimental observations. We express the condition of steady state by the following three additional assumptions:

(A7) $M(x,t) = M$ = constant.

(A8) $f(x,t) = f$ = constant for IRC silicides.

(A9) $f(x,t)\sqrt{t} = g$ = constant for DC silicides.

Assumption (A8) or (A9) provides the additional relationship needed to completely formulate the problem. With (A7), these assumptions identically satisfy Eq. (3) for IRC and DC silicides, so that only Eqs. (4) and (6) need solving for two unknowns: $a_n(x,t)$ and $a_m(x,t)$. With these definitions and assumptions, we present in Figs. 1(a)–1(d) schematic sketches of the sample for $T=0$, $T=1$, $T>1$, and $T=L$.

Using the assumptions (A7)–(A9) and previously defined normalized quantities Eqs. (4) and (6) can be simplified to

$$M\frac{\partial A_m(X,T)}{\partial T} + \frac{\partial A_m(X,T)}{\partial X} = E\,[A_n(X,T) - A_m(X,T)] \tag{7}$$

and

$$\frac{\partial A_n(X,T)}{\partial T} = E\,[A_m(X,T) - A_n(X,T)]\,. \tag{8}$$

The assumption "$M(x,t) = M$" is valid only for the case of IRC silicides. However, for the case of DC silicides, we can assume that $M(x,t)$ is so small that we can neglect even the first order of $M(x,t)$, which is equivalent to assuming

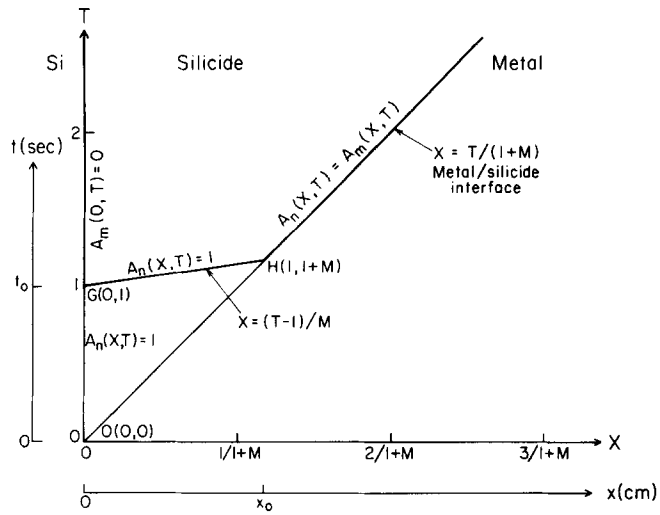

FIG. 2. Two-dimensional (X,T) representation of boundaries where (BC1–BC3) defined.

"$M(x,t) = 0$ = constant." We wish to solve these equations for $t > t_0$ (i.e., $T > 1$), i.e., after all of the ^{31}Si has been incorporated in the silicide. The boundary conditions of the model are (see Fig. 2):

(BC1) $A_m(0,T) = 0$ for $T > 1$. After $T = 1$ the ^{31}Si in the Si substrate is exhausted.

(BC2) $A_n = 1$ on and below line segment GH. For any point $[X_n(T_n),\ T_n]$ on the line segment GH, $X_n(T_n)$ is just the back edge of the moving pure ^{31}Si in the silicide at time T_n, where $1 < T_n < 1 + M$. Therefore the fixed Si at $X_n(T_n)$ has 100% activity when time T is less than or equal to T_n. Note that point G represents the last ^{31}Si in the substrate passing through the Si/silicide interface, and point H the first ^{n}Si reaching the silicide/metal interface.

(BC3) $A_n(X,T) = A_m(X,T)$ at the metal/silicide interface. ^{n}Si and ^{31}Si form silicide with equal probability [assumption (A6)], so that fixed and moving Si have the same activity at the plane where silicide forms.

The solution of this problem is given in Appendix I. Solutions with $M = 0$ and special E's can be understood readily.

(1) $E = 0$ [i.e., $p(c/\lambda) = 0$]. There is no exchange between the moving Si and the fixed Si. The ^{31}Si stays in the silicide that was formed first ($0 < X < 1$, line labeled 0% in Fig. 3).

(2) Very small E $[p(c/\lambda) = c/\lambda \ll x_0 L/\lambda = EL \ll 1]$ (e.g., line labeled 0.01% in Fig. 3). In this case we may neglect atoms that undergo more than one exchange during silicide formation. After $T > 1$ only ^{n}Si atoms cross the Si/silicide interface. The probability that those Si atoms are radioactive at $x = x_0$ is x_0/λ $(= E)$. These radioactive atoms will no more exchange, so that the fraction of radioactive Si in the flux beyond x_0 determines the fraction of the silicide formed, which is E also, everywhere beyond x_0 $[A(X,L) = E$ for $1 < X < L]$. In the region $0 < x < x_0$, the proportion of radioactive Si is decreased [accordingly $A_n(X,L) = 1 - E(L-1)$ for $0 < X < 1$, $L > 1$].

(3) Very large E $[p(c/\lambda) \approx 1]$. This means 100% ex-

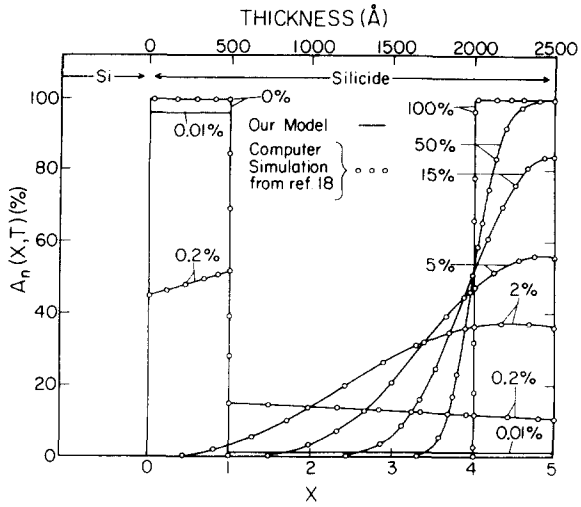

FIG. 3. Comparison of analytical solutions of the first model (Si moves interstitially during silicide formation and exchanges position with the Si in the lattice) (solid lines) with the solutions of a computer simulation[19] (circles) with $x_0 = 500$ Å (thickness of silicide formed by consuming all ^{31}Si), $L = 5$ (thickness of silicide after all metal has been consumed over x_0), $M = 0$ (moving Si density over fixed Si density), and $\Delta x = 5$ Å (depth increment used in simulation). $p(\Delta x/\lambda)$ (exchange probability) and E ($= x_0/\lambda$) are used as parameters: $p(\Delta x/\lambda) = 0\%$, 0.01%, 0.2%, 2%, 5%, 15%, 50%, and 100% correspond to $E = 0$, 0.01, 0.201, 2.04, 5.27, 17.73, 111.8, and infinite, respectively.

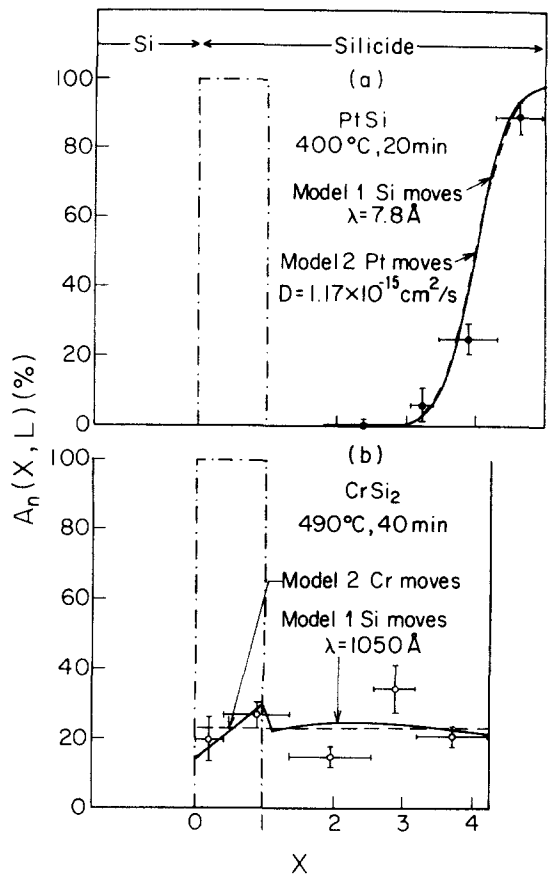

FIG. 4. (a) Comparison of computed profiles with experimental data[19] for PtSi reacted at 400 °C for 20 min. The dash-dotted lines indicate the position of the ^{31}Si if Si atoms were moving interstitially and there were no exchange with the Si in the silicide lattice. The solid line is the solution of our first model which assumes Si atoms were moving interstitially and there were exchanges with fixed Si with $\lambda = 7.8$ Å. The other parameters used in the first model are $x_0 = 390$ Å, $c = 3.1$ Å, $p(c/\lambda) = 87\%$, and $E = 50$. The dashed lines are solution of our second model which assumes metal is the only moving species during silicide formation and ^{31}Si self-diffuses in the silicide with a diffusion constant $\approx 1.17 \times 10^{-15}$ cm^2/s. The solid circles with error bars are the experimental data.[19] (b) Same as (a), but for $CrSi_2$ formed at 490 °C for 40 min: The parameters used in the first model are $E = 0.6$, $x_0 = 630$ Å, $c = 3.3$ Å, $\lambda = 1050$ Å, and $p(c/\lambda) = 0.19\%$. The second model assumes that the diffusion rate for Si is much larger than that of silicide formation. Note that the position defined in the second model has origin at the surface with reverse direction but same unit as shown in the figure.

change. In this case all the ^{31}Si atoms are in the silicide next to the metal/silicide interface (line labeled 100% in Fig. 3).

The present model uses a parameter λ to characterize the exchange rate, while in Ref. 19 an exchange probability over a depth increment Δx is used. The exchange probability is equivalent to the probability $p(\Delta x/\lambda)$ defined in this work. To compare both solutions, λ is chosen such that $p(\Delta x/\lambda)$ equals the exchange probability in a simulation. For $L = 5$ and $M = 0$, Fig. 3 compares solutions of equal exchange probability using that $x_0 = 500$ Å and $\Delta x = 5$ Å. The circles are the numerical results from Ref. 19. The solid lines are the present analytical solutions. The two solutions agree very well.

We were able to fit all of the experimental data that had been fitted by numerical simulation.[19] Two examples are given in Fig. 4. Here the solid lines are the curves fitted to experimental data from Ref. 19 for (a) PtSi [with $E = 50$, $x_0 = 390$ Å, $\lambda = 7.8$ Å, and $c = 3.1$ Å, which correspond to $p(c/\lambda) = 87\%$] and (b) $CrSi_2$ [with $E = 0.6$, $x_0 = 630$ Å, $\lambda = 1050$ Å, and $c = 3.3$ Å, which correspond to $p(c/\lambda) = 0.19\%$]. In our solution we can only specify λ for every radioactive profile. To have an exchange probability $p(\Delta x/\lambda)$ we need to choose a Δx for each silicide. We suggest that $\Delta x = c$, which is the mean distance between fixed Si in the concerned silicide, is the best choice, i.e., we use the probability $p(c/\lambda)$ as the exchange probability for each silicide.

The parameter λ is not the actual length through which a Si atom moves before it exchanges position with a stationary Si atom because the model only considers net movement and ignores thermal random motion. Also the assumption of contrast λ is not valid physically for the dc silicides. The formulation of a physically realistic model is given in Appendix III from which it is seen that thermal random motion introduces additional terms. The fact that the simplified model is able to adequately represent the data is probably due to the significant experimental uncertainty.

B. Model 2

We are also interested in the solution when $t > t_0$. We assume that:

(A1) Metal is the only moving species for silicide formation (interstitially, or substitutionally, or both) during silicide formation.

(A2) Silicon can self-diffuse within the silicide either interstitially or substitutionally with a diffusion constant D during annealing.

The diffusion equation for the ^{31}Si inside the silicide

[i.e., $0 < x < w(t)$ and $t > t_0$] is

$$D\frac{\partial a_n(x,t)}{\partial x^2} = \frac{\partial a_n(x,t)}{\partial t}. \quad (9)$$

The boundary conditions are

$$\frac{\partial a_n(x,t)}{\partial x} = 0 \quad \text{at } x = 0 \quad (10)$$

and

$$D\frac{\partial a_n(x,t)}{\partial x} = -\frac{dw(t)}{dt}a_n(x,t) \quad \text{at } x = w(t). \quad (11)$$

These two boundary conditions result from conservation of ^{31}Si. By definition of t_0 the initial condition for a_n is

$$a_n(0 < x < x_0,\ t = t_0) = 1. \quad (12)$$

Solutions of these equations have been found only for special cases.

(i) If the rate of silicide formation is much greater than that of ^{31}Si self-diffusion and the thickness of silicide is much larger than the ^{31}Si diffusion length, then the boundary condition at the Si/silicide interface has no effect on the solution. Therefore (for $t > t_0$)

$$a_n(x,t) = \int_{-x_0}^{x_0} \exp\{-(x-s)^2/[4D(t-t_0)]\}/\sqrt{4\pi D(t-t0)}ds$$
$$= \{\text{erf}[(x+x_0)/\sqrt{4D(t-t_0)}] - \text{erf}[(x-x_0)/\sqrt{4D(t-t_0)}\}]/2. \quad (13)$$

If we define $A_n(X,t) = a_n(x,t)$ and $B = \sqrt{4D(t-t_0)}/x_0$ then

$$A_n(X,t) = \{\text{erf}[(X+1)/B] - \text{erf}[(X-1)/B]\}/2. \quad (14)$$

(ii) If the diffusion length for ^{31}Si self-diffusion is much larger than the thickness of silicide then

$$a_n(x,t) = x_0/w(t),$$

i.e.,

$$A_n(X,t) = 1/W(t), \quad (15)$$

where $W(t) = w(t)/x_0$.

The profile of the ^{31}Si in the case (i) can be fitted to the experimental data for silicides such as Co_2Si,[17] Ni_2Si,[13] and PtSi.[12] The dashed line in Fig. 4(a) is such a fit for the case of PtSi with $D(t-t_0)/x_0^2 = 0.092$. The ^{31}Si in the case (ii) is uniformly distributed inside the silicide. This agrees with the experimental data for silicides such as $ZrSi_2$, $TiSi_2$, and $CrSi_2$.[17] The dashed line in Fig. 4(b) is a fit for $CrSi_2$. This second model thus also agrees with the observed results.

Thus we find that most of the experimental profiles of ^{31}Si in silicide can be fitted by solutions of both models. This example demonstrates that, in general, a radioactive tracer experiment can not identify the moving species. It takes an inert marker experiment to accomplish this identification. An inert marker, however, can not differentiate between diffusion mechanisms, while tracers can. In general, both types of measurements are needed to characterize the moving species and the diffusion mechanisms.[21]

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APPENDIX I

To solve Eqs. (7) and (8) with (BC1–BC3) we use the following variables:

(T1) $x_c = EX$,

(T2) $t_c = ET - EMX$,

(T3) $A_c = A_n \exp(t_c + x_c - E)$,

and

(T4) $C_c = A_m \exp(t_c + x_c - E)$.

Using x_c and t_c we can rewrite Eqs. (7) and (8) as

$$\frac{\partial A_c}{\partial t_c} = C_c \quad (16)$$

and

$$\frac{\partial C_c}{\partial x_c} = A_c. \quad (17)$$

The boundary conditions can also be rewritten (see Fig. 5):

(BC1) $C_c = 0$ for $x_c = 0$ and $t_c > E$,

(BC2) $A_c = \exp(x_c)$ on GH (i.e., $t_c = E$ and $x_c < E$),

(BC3) $A_c = C_c$ at the metal/silicide interface (i.e., $x_c = t_c$).

Equations (16) and (17) are a hyperbolic system with (BC1) and (BC2) defined on its characteristic lines. If the (BC3) were also defined on the characteristic line we could easily solve this problem. However, since Eqs. (16) and (17) and (BC3) are symmetric with respect to A_c and C_c we can

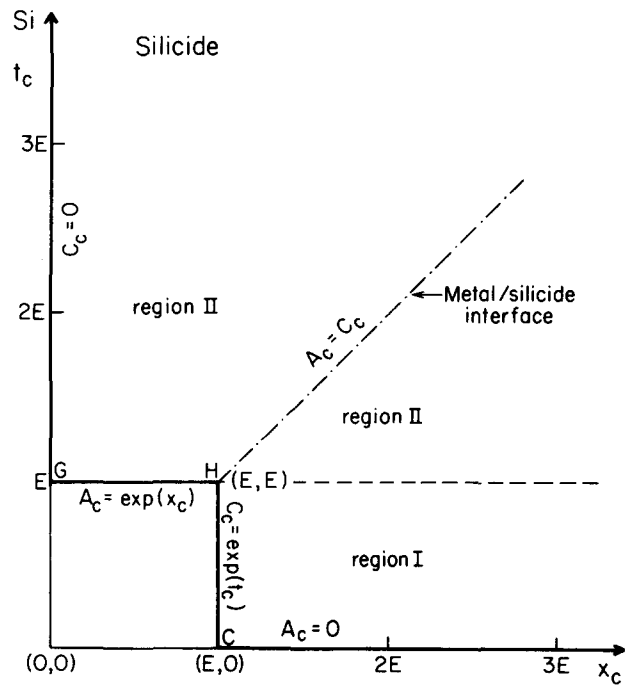

FIG. 5. Two-dimensional (x_c,t_c) representation of boundaries where (BCA1–BCA4) defined.

change (BC1–BC3) to the following (see Fig. 5):

(BCA1) $C_c = 0$ for $x_c = 0$ and $t_c > E$,
(BCA2) $A_c = \exp(x_c)$ on GH,
(BCA3) $C_c = \exp(t_c)$ on HC,
(BCA4) $A_c = 0$ for $t_c = 0$ and $x_c > E$.

Now all the boundary conditions are defined on the characteristic lines. The problem can be solved by Laplace transformation. We define

$$LFun(s) = \int_0^\infty Fun(x_c)\exp(-sx_c)\,dx_c\,, \tag{18}$$

where $Fun(x_c)$ is a function of x_c. The inverse transformation $L^{-1}[LFun(s)]$ is equal to $Fun(x_c)$ for $x_c > 0$ and equal to 0 for $x_c < 0$. Since we are only interested in the region $t_c > E$, we can let $A_c = C_c = 0$ in the region $(0 < x_c < E,\ 0 < t_c < E)$.

In region I $(x_c > 0,\ 0 < t_c < E)$, after Laplace transformation with respect to x_c, Eqs. (16) and (17) become

$$\frac{\partial LA_c}{\partial t_c} = LC_c \tag{19}$$

and

$$sLC_c - \exp(t_c - sE) = LA_c\,. \tag{20}$$

These can be solved:

$$LA_c = [\exp(t_c) - \exp(t_c/s)]\exp(-sE)/(s-1)\,, \tag{21}$$

$$LC_c = [\exp(t_c) - \exp(t_c/s)/s]\exp(-sE)/(s-1)\,. \tag{22}$$

Using these two solutions along $t_c = E$ and (BCA2) as boundary conditions we can find the solution in region II ($t_c > E$ and $x_c > 0$) as follows:

$$LA_c = \exp[(t_c - E)/s]/(s-1) - \exp(t_c/s) \times \exp(-sE)/(s-1)\,, \tag{23}$$

$$LC_c = LA_c/s\,. \tag{24}$$

If we define

$$F(x_c,t_c) = L^{-1}[\exp(t_c/s)/(s-1)] \quad \text{for } t_c > 0$$
$$= 0 \quad \text{for } t_c < 0\,,$$

(note that from definition $F(x_c,t_c) = 0$ if $x_c < 0$) then

$$A_c = F(x_c,t_c - E) - F(x_c - E,t_c)$$

and

$$C_c = F(t_c,x_c - E) - F(t_c - E,x_c) + \exp(x_c + t_c - E)[1 - U(x_c - E)]\,,$$

where

$$U(x_c) = 0 \quad \text{for } x_c < 0,$$
$$U(x_c) = 1/2 \quad \text{for } x_c = 0,$$

and

$$U(x_c) = 1 \quad \text{for } x_c > 0.$$

To solve this problem we simply need to know

$$F(x_c,t_c) = \sum_{n=0}^{\infty} (x_c,t_c)^{n/2} I_n(2\sqrt{t_c x_c})\,, \tag{25}$$

where $I_n(x)$ is the first kind nth order modified Bessel function, or

$$F(x_c,t_c) = \exp(x_c + t_c) - \sum_{n=1}^{\infty} \frac{t_c^n}{n!} \sum_{k=1}^{n} \frac{x_c^{k-1}}{(k-1)!} \tag{26}$$

or

$$F(x_c,t_c) = \exp(x_c + t_c)/2 + I_0(2\sqrt{x_c t_c})/2 + \exp(x_c + t_c)(x_c - t_c)/(4\sqrt{x_c t_c}) \times \int_0^{2\sqrt{x_c t_c}} I_0(z)\exp\left[-(\sqrt{x_c/t_c} + \sqrt{t_c/x_c})z/2\right]dz\,. \tag{27}$$

From this we get the solution of this problem $(T > 1)$:

$$A_n(X\,T) = \exp\{-E[T - 1 + X(1-M)]\} \times \{F[EX,E(T-1) - EMX] - F(EX - E,ET - EMX)\} \tag{28}$$

and

$$A_m(X,T) = \exp\{-E[T - 1 + X(1-M)]\} \times \{F[ET - EMX,E(X-1)] - F[E(T-1) - EMX,EX]\} + 1 - U[E(X-1)]\,. \tag{29}$$

From Eqs. (25)–(28) we can write down some solutions with special E (for simplicity we set $M = 0$ and $L > 1$)

(1) $E = 0$:

$$A_n(X,L) = 1 \quad \text{for } 0 < X < 1,$$
$$= 0 \quad \text{for } 1 < X < L\,. \tag{30}$$

(2) Small E (the second and higher orders of E can be neglected):

$$A_n(X,L) = 1 - E(L-1) \quad \text{for } 0 < X < 1$$
$$= E \quad \text{for } 1 < X < L\,. \tag{31}$$

(3) Large E:

$$A_n(X,L) = U(X - L + 1) + \exp\left[-E(\sqrt{X} - \sqrt{L-1^2}\right]G(X,L-1) + \exp\left[-E(\sqrt{X-1} - \sqrt{L-2})^2\right]G(X-1,L-2)\,, \tag{32}$$

where

$$G(x,y) = \frac{1}{\pi}\int_0^{\pi/2} \frac{\exp\{-E\,2\sqrt{xy}[1 - \cos(z)]\}[y - \sqrt{xy}\cos(z)]}{x + y - 2\sqrt{xy}\cos(z)}\,dz\,. \tag{33}$$

(4) Infinite E:

$$A_n(X,L)=0 \quad \text{for } 0<X<L-1$$
$$=1 \quad \text{for } L-1<X<L. \tag{34}$$

APPENDIX II

In this Appendix we want to calculate the exchange probability $p(d,\lambda)$ which is defined as the fractional change of the integrated fixed activity of a layer of finite thickness d of silicide made up initially of pure ^{31}Si after a flux of pure ^{n}Si has passed whose integrated flux equals the amount of Si in that silicide layer. For simplicity we will assume $M=0$ during calculation.

If we let pure ^{n}Si atoms move through a fixed layer of silicide made up of pure ^{31}Si initially, i.e., $A_n(X,T=1)=1$, of thickness $x_0>d$ then at $T=1+d/x_0$, i.e., the integrated flux of Si atoms passing through the first layer with thickness d is equal to that of Si atoms in the first layer of the silicide, the fractional change of the total activity of the fixed Si in the first layer is $[=p(d,\lambda)]$:

$$p(d,\lambda)=1-\int_0^{d/x_0} A_n(X,T=1+d/x_0)dX/(d/x_0). \tag{35}$$

Using the same calculation as in Appendix I [see Eq. (28)] we can get (for $0<X<d/x_0$)

$$A_n(X,T=1+d/x_0)$$
$$=\exp[-E(X+d/x_0)]F(EX,Ed/x_0).$$
$$=\exp[-(x/d+1)d/\lambda\,]F(x/\lambda,d/\lambda). \tag{36}$$

Therefore

$$p(d,\lambda)=1-\int_0^1 \exp[-(1+y)d/\lambda\,]F(yd/\lambda,d/\lambda)dy$$
$$=1-\exp(-2d/\lambda)[I_0(2d/\lambda)+I_1(2d/\lambda)]$$
$$=\sum_{n=1}^{\infty}\{(-1)^{n+1}(d/\lambda)^n(2n)!/[(n!)^2(n+1)!]\}$$
$$=p(d/\lambda). \tag{37}$$

Note that

$$p(d/\lambda)\approx d/\lambda \quad \text{for } d/\lambda \ll 1$$

and that

$$p(d/\lambda)\approx 1-\sqrt{\lambda/(\pi d)} \quad \text{for } d/\lambda \gg 1.$$

APPENDIX III

Physically the total flux of moving Si is due to the diffusion of moving Si, therefore by Fick's law

$$f(x,t)=-D\frac{\partial m(x,t)}{\partial x}, \tag{38}$$

where D is the diffusion constant of moving Si in silicide. From the same reason the flux of the ^{31}Si, $^{*}f(x,t)$, can be represented by

$$^{*}f(x,t)=-D\frac{\partial[m(x,t)a_m(x,t)]}{\partial x}$$
$$=f(x,t)a_m(x,t)-Dm(x,t)\frac{\partial a_m(x,t)}{\partial x}. \tag{39}$$

The continuity equation for the total moving Si is not changed [see Eq. (3)]. But that for the moving ^{31}Si becomes

$$2f(x,t)\frac{\partial a_m(x,t)}{\partial x}-Dm(x,t)\frac{\partial^2 a_m(x,t)}{\partial x^2}$$
$$=-n\frac{\partial a_n(x,t)}{\partial t}-m(x,t)\frac{\partial a_m(x,t)}{\partial t}. \tag{40}$$

Comparing this equation with Eq. (4) we can see that there are two additional terms are added to this new equation. Therefore the assumption that the flux of moving Si is purely convective used in the first model is not rigorously justified.

Concerning the exchange between a moving Si and a stationary Si we have assumed the constant mean free length (λ). However, a constant mean free time (τ:the average time that a diffusing Si atom exchanges position with a fixed Si atom) is a better assumption than a constant mean free length physically. By assuming a constant τ, we simply replace the term $f(x,t)/\lambda$ in Eq. (6) by $m(x,t)/\tau$, i.e.,

$$\frac{\partial[na_n(x,t)]}{\partial t}=[a_m(x,t)-a_n(x,t)]m(x,t)/\tau. \tag{41}$$

Numerically, the four unknown functions, $f(x,t)$, $m(x,t)$, $a_n(x,t)$, and $a_m(x,t)$, can be solved by using Eqs. (3), (38), (40), and (41). However, it is difficult to solve this problem analytically. We therefore just formulate the problem without solving it.

[1]By "moving species for silicide formation" we mean the species that moves with respect to an inert marker fixed to the silicide lattice.
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